

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 709 030 A1

(12)

EUROPÄISCHE PATENTANMELDUNG

(43) Veröffentlichungstag:

01.05.1996 Patentblatt 1996/18

(51) Int. Cl.⁶: **A22C 13/00**

(21) Anmeldenummer: **95116658.6**

(22) Anmeldetag: **23.10.1995**

(84) Benannte Vertragsstaaten:

AT BE CH DE DK ES FR GB IT LI NL SE

(30) Priorität: **31.10.1994 DE 4438961**

(71) Anmelder: **HOECHST AKTIENGESELLSCHAFT
D-65926 Frankfurt am Main (DE)**

(72) Erfinder:

- **Hammer, Klaus-Dieter, Dr.
D-55120 Mainz (DE)**
- **Grolig, Gerhard, Dr.
D-64546 Mörfelden-Walldorf (DE)**
- **Beissel, Dieter
D-65203 Wiesbaden (DE)**

(54) **Wursthüllen aus thermoplastischer Stärke und Verfahren zu deren Herstellung**

(57) Die vorliegende Erfindung betrifft die Verwendung von thermoplastisch verarbeitbarer Stärke für Wursthüllen sowie ein Extrusionsverfahren zu ihrer Herstellung.

EP 0 709 030 A1

THIS PAGE BLANK (USPTO)

Sausage casings made of thermoplastic starch and process for the production thereof

5 The present invention relates to a tubular sausage casing and to an extrusion process for the production thereof.

10 In sausage production, virtually only the collagen casings (= membrane fibrous casings), the cellulose hydrate casings and casings made of synthetic polymers have achieved importance. The latter generally comprise polyamide, polyethylene, polypropylene, poly(ethylene terephthalate), poly(butylene terephthalate) or poly(vinylidene chloride) copolymers. Other synthetic 15 casings, such as casings made of protein- or acrylate-coated fabric are scarcely worthy of mention.

20 Collagen casings and cellulose hydrate casings have the advantage that they are produced from renewable raw materials, are biodegradable and thus can be composted. The processes for their production, however, are generally highly complex and environmentally polluting. Thus, for example, synthetic casings based on cellulose hydrate are produced by the viscose process, in which 25 sodium hydroxide solution and carbon disulfide are used.

30 The casings produced from synthetic polymers can be produced simply and inexpensively by extrusion, but they are not biodegradable and must therefore be disposed of in a complex manner.

35 The object was therefore to provide a sausage casing which combines in itself the advantages of the known casings. It should be suitable for all sausage types, it should be producible simply and in an environmentally friendly manner from renewable raw materials and be biodegradable.

The object has been achieved by the use of starch which can be processed like a thermoplastic.

5 Natural starch, such as potato starch, corn starch or
cereal starch, is composed of macromolecules and is
highly inhomogeneous. The macromolecules occur in the
form of α -helix. On heating, the natural starch decom-
poses before it reaches the melting temperature. If
water is added in advance, a composition which can be
10 processed like a thermoplastic is obtained. Since
water, because of its low boiling point, is not so
expedient in processing terms, additives such as
glycerol, ethylene glycol or propylene glycol are more
suitable, since they have a higher boiling point. The
15 proportion of these additives should be at least 5 % by
weight, based on the weight of the dry starch.

Thermoplastic starch, process for the production
thereof and shaped bodies produced therefrom are
20 disclosed by WO 90/05161 and 90/10019. The applications
specified were: filler or formulation aid in
thermoplastics and thermosets or support material for
active compounds, such as pharmaceutical active
compounds, or reagents such as flocculents for waste
25 water. It is stated that extruded films of
thermoplastic starch can be laid out in a low-water
environment or on a water-permeable underlay and bind
water. This is said to improve the efficiency of soil
irrigation in arid regions. There has been no previous
30 indication that thermoplastic starch could be suitable
for the production of sausage casings, especially those
which cover a broad field of application.

The starting material used for the production of the
35 sausage casings is thermoplastic starch which is
disclosed in the said WO publications. This starch
generally occurs as granules or in the form of beads.
It is critical for the production of sausage casings
having optimal properties that the natural starch is

converted into the amorphous state with abolition of the α -helix structure. This is successfully achieved, for example, by heating and mechanical mixing, expediently in a kneader or in a single- or twin-screw extruder. In order to achieve melting of the starch below the decomposition temperature, the known plasticizers such as water, butane-1,3-diol, glycerol, diglycerol, N,N-dimethylurea, sorbitol or citrate are used.

10

When water is used as plasticizer, this is used in an amount of about 15 to 25 % by weight, preferably about 17 % by weight, based in each case on the weight of the plasticized starch. The temperature should be about 100 to 130°C. When glycerol is used as plasticizer, an amount of 0.5 to 20 % by weight, preferably 8 to 16 % by weight, is sufficient, again based on the weight of the starch in each case. The temperature in this case is expediently somewhat higher. 150 to 170°C is favorable. The crystalline proportion in the thermoplastic starch should at any event be less than 5 % by weight.

In order to adapt the casings to the various sausage types, suitable substances are added to the granulated thermoplastic starch. These are in particular fibers which increase the mechanical strength. Such sausage casings are novel and are part of the present invention.

30

Casings for raw sausage, in addition to the thermoplastic starch, expediently contain

5 to 30 % by weight,	preferably 10 to 20 % by weight, fiber reinforcement, preferably cotton combings,
3 to 25 % by weight,	preferably 5 to 15 % by weight, protein, preferably gelatin, casein or wheat pro-

tein, and

2 to 15 % by weight, preferably 3 to 10 % by weight, crosslinker, preferably a dicarboxylic acid, a dialdehyde, a diisocyanate or a diepoxide.

5

These and also the following figures in % by weight relate to the weight of the plasticized starch (total weight of starch + plasticizer).

- 10 In order to satisfy the requirements for scalded-meat sausage and cooked-meat sausage and cooked ham, fiber reinforcement is necessary. Cotton linters, synthetic fibers or regenerated fibers (= fibers from regenerated cellulose) are particularly suitable therefor. The
15 proportion of fiber reinforcement is generally 3 to 25 % by weight, preferably 5 to 15 % by weight.

- A further quality improvement - depending on the application - may be achieved by additional synthetic polymers, preferably soft and ductile polyamides, polyesters, polyolefins, ethylene/ethylacrylate/maleic anhydride copolymers or polyvinylpyrrolidone (PVP). The polyolefins are preferably low-density polyethylenes or polypropylenes. The proportion of the synthetic
20 polymers is expediently 5 to 50 % by weight, preferably 10 to 40 % by weight. Crosslinkers increase the water resistance. Their proportion, in the casings for scalded-meat sausage and cooked ham, is 2 to 20 % by weight, preferably 3 to 12 % by weight. Preferred
25 crosslinkers have already been mentioned under raw sausage casings. Lubricants can facilitate extrusion. For this purpose, the animal or vegetable fats or lecithins already disclosed in the abovementioned WO 90/05161 are especially suitable. Lubricants improve
30 the peelability and likewise the water resistance. Their proportion is generally 2 to 12 % by weight, preferably 3 to 6 % by weight.
35

Fiber-free, transparent casings, in addition to the

thermoplastic starch, expediently contain alginate, chitosan, extrudable cellulose derivatives (preferably cellulose acetate or cellulose propionate) and/or proteins (preferably gelatin). The proportion of additional constituents is from 5 to 70 % by weight, preferably 20 to 50 % by weight. To improve the mechanical stability and the water resistance and resistance to boiling, the abovementioned crosslinkers can additionally be present in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight. The suppleness of the stretched sausage casing can be further improved by a softener, preferably glycerol or citric ester. The proportion of the added softener is 3 to 30 % by weight, preferably 5 to 20 % by weight.

A process for the production of starch-based sausage casings is likewise subject-matter of the present invention. The process comprises molding the mixture of thermoplastic starch and the remaining constituents using an extruder, preferably a single- or twin-screw extruder and a ring die attached thereto which is heated to 100 to 140°C, preferably 105 to 120°C to give a tubular casing, inflating this and stretching it in a ratio of 1:2 to 1:10, preferably 1:3 to 1:5, based on the surface area in each case. A homogeneous melt thus forms in the extruder. During stretching by blow molding, the casing is preferably inflated using air.

In a further step, an impregnation or coating can subsequently be applied internally and/or externally. It serves in particular to improve the sausage emulsion adhesion or to increase resistance to mold.

The starch-based sausage casings exhibit all of the positive properties of cellulose hydrate casings. The impregnations or coatings known from the cellulose hydrate casings are generally also suitable for the starch casings. In particular, layers can also be applied which act as a barrier for oxygen and/or water

vapour. The starch casings can be adapted by this means to all important sausage types.

Production of the thermoplastic starch

5 100 kg of potato starch were dried in vacuo until the water content was less than 0.3 % by weight. The starch was then mixed with 50 kg of glycerol (99 % by weight pure) in a kneader at a temperature of 160 to 190°C. To abolish the helix structure, the melt produced in this
10 process was kept for about 2 hours at a temperature of 170°C. It was then extruded and granulated. Even after relatively long storage, the starch remained virtually completely amorphous in the granules.

15 Example 1

To produce a raw sausage casing having fiber reinforcement,

20 75.0 kg of the abovedescribed granules (50 kg of starch + 25 kg of glycerol) were mixed with
10.0 kg of cotton linters,
10.0 kg of gelatin,
2.5 kg of adipic acid and
25 2.5 kg of sunflower seed oil,

extruded at 110 to 120°C and stretched longitudinally and transversely in the ratio of 1:8, based on the surface area. In this manner, a tube of caliber 60 (= 30 60 mm) was obtained, having a wall thickness of 90 µm.

The tube was then laid flat, wound up and then gathered together to form concertinaed casings or finished to form sections tied off at one end.

35

In order to test the mechanical properties of the casing, it was soaked in water and subjected to a pressure test. It did not burst until a pressure of 65 to 72 kPa (bursting pressure) was reached. The static

extension at 21 kPa was 65 to 75 mm.

5 In order to test the applicability, the casings were filled with salami emulsion and subjected to the usual ripening process. During ripening, the casing did not detach from the emulsion, i.e. "disconnection" of the casing did not occur. The peelability of the ripened salami was evaluated as "2" (rating scale of 1 to 6; 1 = very good peelability, 6 = no longer peelable).

10

Example 2

To produce a casing for scalded-meat\ and cooked-meat sausage and cooked ham,

15 75.0 kg of the abovedescribed granules were mixed with
 7.5 kg of cotton linters,
 20.0 kg of a soft, supple copolyamide,
 5.0 kg of glyoxal and
20 7.5 kg of lecithin.

The mixture was homogenized by kneading for about half an hour at 185°C and was then extruded through a ring die for caliber 60. By blow-molding, the tubular casing
25 was then stretched longitudinally and transversely in the ratio of 1:6 (based on the surface area). The wall thickness of the stretched tube was 85 µm. The bursting pressure of the water-soaked casings was 72 kPa, the static extension at 21 kPa was 68 mm.

30

A water-soaked casing piece tied off at one end was then filled with meat sausage emulsion. The casing could be removed without difficulty from the conventionally scalded and smoked sausage.

35

Example 3

To produce a fiber-free, transparent sausage casing,

75.0 kg of the abovedescribed granules were

mixed with
20.0 kg of gelatin,
10.0 kg of chitosan
7.5 kg of glyoxal,
5 5.0 kg of triethyl acetylcitrate (^(R)Citroflex
A4) and
2.5 kg of lecithin,

processed in an extruder at 178°C to give a homogeneous
10 melt and extruded through a ring die for caliber 75.
The tubular casing was then stretched longitudinally
and transversely by blow-molding in the ratio of 1:8
(based on the surface area), then laid flat and wound
up. The wall thickness of the stretched casing was 108
15 µm. The bursting pressure of the water-soaked casing
was 30 kPa. The static extension at 15 kPa was 88 to 92
mm.

Sections of the tubular casing tied off at one end were
20 filled with "Bierwurst" emulsion. After scalding and
smoking, the casing could be peeled off easily from the
emulsion.

Example 4

25 A fiber-free casing could also be produced with starch
which had been plasticized with water instead of
glycerol. For this purpose,

100.0 kg of potato starch were mixed with
30 7.0 kg of water,
1.0 kg of sunflower seed oil and
0.5 kg of lecithin.

The mixture was melted in a kneader at 165°C and
35 homogenized for 1 hour. The melt was then extruded and
granulated.

60.0 kg of the granules thus produced were then
mixed with

10.0 kg of gelatin,
10.0 kg of chitosan,
10.0 kg of glycerol,
7.5 kg of glyoxal and
5 5.0 kg of sunflower seed oil.

The mixture was converted into a homogeneous melt using an extruder and was extruded through a ring die for caliber 80. By blow-molding in the ratio 1:6 (based on
10 the surface area), the tubular casing was then stretched longitudinally and transversely. The casing was then laid flat and rolled up. The wall thickness of the stretched casing was 95 μm . The bursting pressure of the water-soaked casing was 22 kPa. The static
15 extension at 15 kPa was 95 to 100 mm.

Casing part-pieces tied off at one end were filled with long-keeping-sausage emulsion. The sausages ripened without defect and could be easily peeled.

Patent Claims

1. Use in sausage casings of starch which can be processed like a thermoplastic.
- 5 2. A thermoplastic-starch-based casing for raw sausage, which casing, apart from thermoplastic starch, contains
10 5 to 30 % by weight of fiber reinforcement,
3 to 25 % by weight of protein and
2 to 15 % by weight of crosslinker.
- 15 3. A thermoplastic-starch-based casing for scalded-meat sausage and cooked ham which, apart from thermoplastic starch, contains 3 to 25 % by weight of a fiber reinforcement.
- 20 4. The casing as claimed in claim 3, wherein it additionally contains synthetic polymers, cross-linkers and/or lubricants.
- 25 5. The casing as claimed in claim 4, wherein the proportion of the synthetic polymers is 5 to 50 % by weight, preferably 10 to 40 % by weight, the proportion of the crosslinkers is 2 to 20 % by weight, preferably 3 to 12 % by weight and the proportion of the lubricants is 2 to 12 % by weight, preferably 3 to 6 % by weight.
- 30 6. A thermoplastic-starch-based, fiber-free, transparent sausage casing which, in addition to thermoplastic starch, contains alginate, chitosan, extrudable cellulose derivatives and/or proteins
35 in a proportion of from 5 to 70 % by weight.
7. The casing as claimed in claim 6, wherein it contains crosslinkers in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight,

and/or softeners in a proportion of from 3 to 30 %
by weight, preferably 5 to 20 % by weight.

- 5 8. A process for the production of sausage casings as
claimed in claims 2 to 7, which comprises molding
the mixture of thermoplastic starch and the
remaining constituents using an extruder and a
ring die attached thereto which is heated to 100
to 140°C to give a tubular casing, then inflating
10 this and stretching it in the ratio 1:2 to 1:10,
based on the surface area in each case.
- 15 9. The process as claimed in claim 8, wherein the
tubular casing is stretched in the ratio of 1:3 to
1:5, based on the surface area in each case.
- 20 10. The process as claimed in claim 8 or 9, wherein an
impregnation or coating is applied internally
and/or externally to the stretched sausage
casings.

THIS PAGE BLANK (USPTO)